# SUMMARY AND SYNTHESIS REPORT ON RADIONUCLIDE RETARDATION FOR THE YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT

## Yucca Mountain Site Characterization Program Milestone 3784M

by

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## ABSTRACT

This report is a detailed summary of laboratory and modeling studies performed by or for Los Alamos National Laboratory in support of the Yucca Mountain Site Characterization Project on the mechanisms by which radionuclide transport from the proposed repository for high-level nuclear waste at Yucca Mountain, Nevada, is retarded or enhanced by sorption, diffusion, solubility limits, and colloid transport. As direct input into these studies, the report also includes a summary of what has been accomplished in the development of a model for groundwater chemistry at Yucca Mountain. Chapter I introduces background material, including discussions of the site of the potential repository, the overall approach to this aspect of site characterization, the chemical nature of the on-site waters, and the types and variability of minerals in the rock matrix and on fracture surfaces. Chapter II discusses the groundwater chemistry of the saturated and unsaturated zones and the different types of processes that influence that chemistry. The first line of defense against radionuclide transport, the limits on solubilities, is discussed in Chp. III. The second line of defense, the sorption of radionuclides onto the surrounding tuffs, is discussed in Chp. IV. A summary of what is known for the sorption of all the key radionuclides and a presentation of extensive batch-sorption measurements for uranium, plutonium, and neptunium are included. The effect that organic coatings on mineral surfaces has on the sorption of actinides is also covered. Cation-exchange and surface-complexation models that can explain the sorption data are discussed. Chapter V covers dynamic-transport studies that complement and extend the batch-sorption work. These studies include experiments with crushed-rock columns, solid-rock columns, and fractured columns, as well as work on colloid-facilitated transport of radionuclides. Chapter VI summarizes both the work using rock beakers and diffusion cells to study diffusion in saturated tuff and the work using centrifuge-induced flow to study diffusion through unsaturated tuff. The main conclusions of all of this work are presented in Chp. VII, which also includes a summary of research performed as part of the Biological Sorption and Transport Task on how microorganisms affect radionuclide transport at Yucca Mountain.

# I. INTRODUCTION

## A. THE POTENTIAL REPOSITORY SITE

Yucca Mountain, in southern Nevada, is the potential site for a repository for high-level radioactive waste from commercial power and nuclear defense industries. Yucca Mountain is composed of a thick (greater than 1.5 km) sequence of ash-flow tuff units and subordinate lavas (Fig. 1). Most units retained enough heat after deposition to develop densely welded, devitrified interiors in which the original glass particles consolidated and crystallized to a high-temperature assemblage of feldspars and silica minerals (Levy 1992). Levy reports that the upper and lower margins of the units remain vitric; thinner, bedded tuffs between the main ash flows are also vitric and nonwelded. In the middle and lower units, most glassy tuffs have diagenetically altered to hydrous assemblages dominated by zeolites.

The location of the proposed repository is approximately 300 m below the surface of the mountain and 200 to 400 m above the static water level (Levy 1992). The presence of the thick zeolitic tuffs in continuous zones throughout the region was a major consideration for choosing Yucca Mountain as a potential repository site (Johnstone and Wolfsberg 1980); the zeolites could sorb important radionuclides from groundwaters and thus retard the movement of radioactivity from the repository site. The potential repository at Yucca Mountain would be located within the densely welded devitrified tuff of the Topopah Spring Member of Paintbrush Tuff with a vitrophyre underlying this location.

Because the proposed location is in the unsaturated zone, conditions are oxidizing. The Yucca Mountain region is in the shadow of the Sierra Nevada range and receives little rainfall. Estimates of groundwater flux are extremely low, and the site is remote, located at the western edge of the Nevada Test Site, approximately 100 miles northwest of Las Vegas, Nevada.

One major aspect of characterizing the site and assessing its suitability as a repository is to determine the extent to which the natural geochemical barriers will prevent the release of radionuclides from the underground repository. The retardation of radionuclides by sorption onto tuffs is of major importance, and one of the main goals of our research at the Los Alamos National Laboratory is to obtain data and to develop models for the sorption behavior of key radionuclides under the physical and chemical conditions anticipated at the proposed repository. Such work involves detailed investigation and modeling of the interactions between solid-rock materials and radionuclides in aqueous solutions.

Several related studies support and complement the main sorption research. The characterization and modeling of the chemistry of Yucca Mountain groundwaters is vital. Other studies include the role of diffusion in Yucca Mountain tuff, the limits imposed by the solubilities of the radionuclides, the potential transport of radionuclides by colloids, the effects of organic compounds on sorption, and radionuclide transport through fractures in the tuff. The validation of the results of static batch-sorption studies with dynamic transport studies is also extremely important.

This report summarizes the laboratory and modeling studies carried out or directed by scientists at Los Alamos for this effort. Specifically, we report on investigations of the mechanisms by which radionuclide transport is retarded or enhanced by sorption, diffusion, solubility limits, and colloid transport.

The role of microbial activity on the transport of radionuclides is described in a Los Alamos report on Yucca Mountain Site Characterization Program milestone 3663 (Hersman 1996).

An assessment of the potential for radionuclide retardation at Yucca Mountain must be based on an understanding of the petrology and mineralogy of
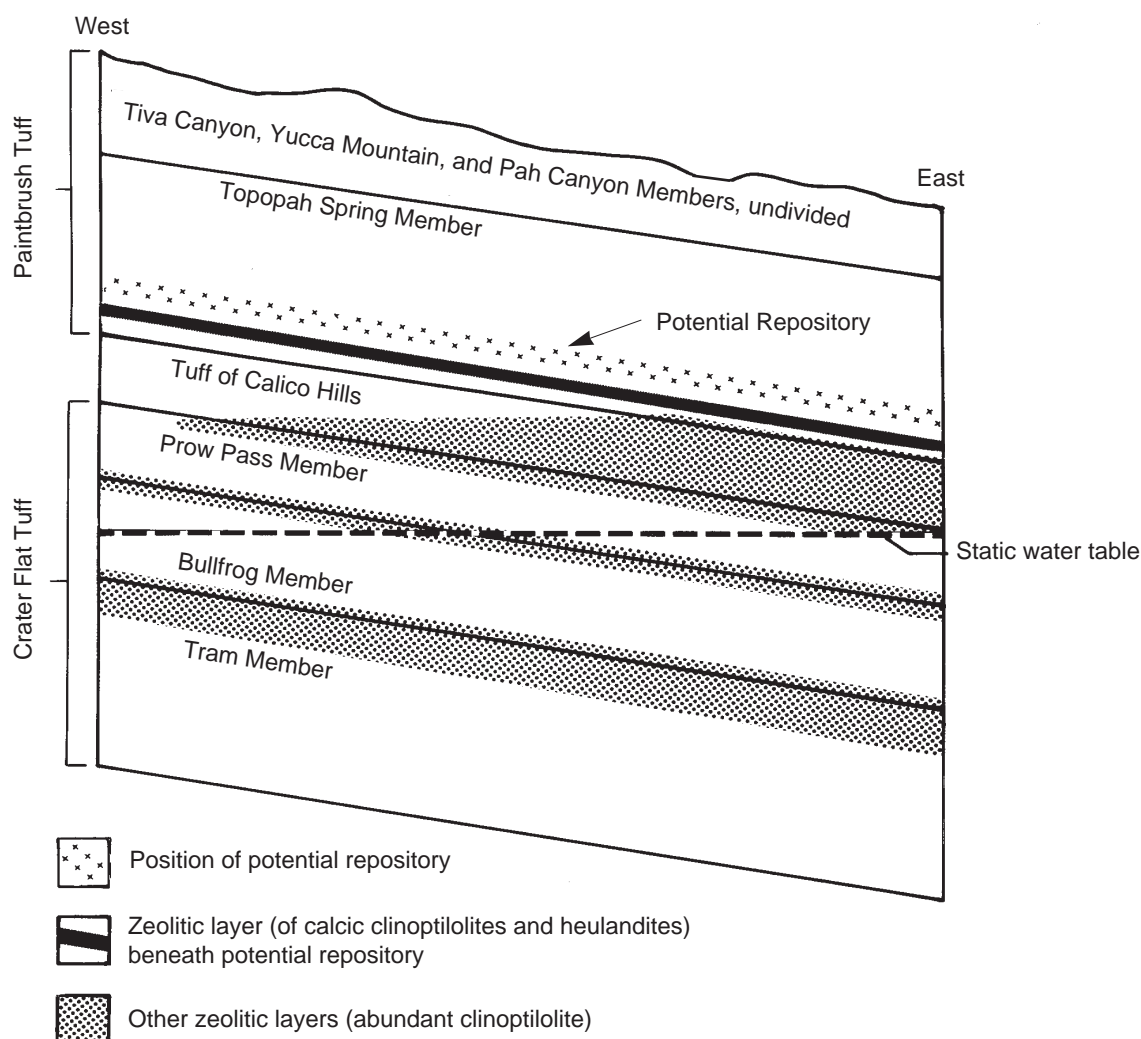
**Figure 1. Cross Section of Yucca Mountain.** This schematic of an east-west cross section of Yucca Mountain shows the vertical position of the potential repository in relation to the static water table and the principal layers of zeolitic tuffs (from Broxton 1986).

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the proposed repository horizon and the underlying strata. This work is summarized in a series of Yucca Mountain Site Characterization milestone reports (Bish et al. 1996a; Levy et al. 1996; Carey et al. 1996).

**Regulatory Limits for the Release of Radionuclides**

The types of radioactive waste that may be emplaced in the proposed high-level nuclear waste repository include spent fuel, high-level (reprocessing) waste, and high-level defense waste.

Oversby (1987) has evaluated compositions and likely inventories of spent fuel and has provided lists of those radionuclides for which the performance of a geological repository site will be critical with respect to meeting the regulatory release limits. Oversby compared the maximum annual release rates from an engineered-barrier system allowed by the Nuclear Regulatory Commission (NRC) regulations of 10 CFR 60 (NRC 1980) with integrated release limits to the accessible environment allowed by the Environmental Protection Agency (EPA) regulations of 40 CFR 191 (EPA 1982). In effect, Oversby assumed the boundary to

3

the accessible environment and the boundary to the engineered barrier to be one and the same. The "important radionuclides" were identified as those for which the allowed NRC annual release rates from the engineered barrier system resulted in integrated release rates to the accessible environment that exceeded the EPA release limits.

Table 1 lists the "important radionuclides" resulting from this evaluation in order of the degree to which they exceed the EPA release limits. Note that this listing is independent of the characteristics of the engineered-barrier system and of the site—it is a direct result of the composition of any quantity of the emplaced waste and the combined NRC and EPA regulations.

Unless the engineered-barrier system itself is designed to provide compliance with the EPA regulations, site characteristics between the boundary of the engineered barrier and the boundary of the accessible environment must be called on for such compliance. The site characteristics that could ultimately determine the rate at which radionuclides are released to the environment (Fig. 2) include: 1) the solubilities of compounds of the important radionuclides that are stable in groundwaters located between the repository horizon and the accessible environment, 2) the rate and volume of water and air movement through the repository to the accessible environment, 3) the dispersion rates for radionuclides in the groundwater and air-flow systems associated with the site, 4) the sorption of radionuclides to immobile and mobile (for example, colloidal) surfaces present in the groundwater and air-flow systems associated with the site, and 5) the decay of the radionuclides during transport.

**Stratigraphy of Yucca Mountain**

Figure 1 gives the names of the main layers of Yucca Mountain tuff and shows their relationship to the static water table and the intervals of zeolites. Figure 3 is a more detailed, scaled view of Yucca Mountain that also shows the positions of the drill holes used to develop the stratigraphic pic-

### Table 1. Important Radionuclides and the Reduction Factor Required to Meet Maximum Allowed Releases

| Element | Reduction factor* |
|---------|-------------------|
| Americium | 18,300 |
| Plutonium | 12,300 |
| Thorium | 457 |
| Uranium | 52 |
| Curium | 46 |
| Carbon | 46 |
| Neptunium | 46 |
| Radium | 38 |
| Nickel | 13 |
| Iodine | 9 |
| Cesium | 5 |
| Tin | 5 |
| Selenium | 5 |
| Zirconium | 5 |
| Niobium | 5 |
| Technetium | 3 |
| Palladium | 3 |

*Assuming each radionuclide accounts for not more than 0.035 of total U.S. EPA limit and assuming no precipitation.

ture. Samples from the cores of a number of these drill holes were used throughout the research reported on here.

The stratigraphic units in Yucca Mountain include partially-welded to densely-welded devitrified tuff, moderately-welded to densely-welded vitrophyre, and nonwelded vitric tuff that in places has been extensively altered to zeolite minerals (Scott et al. 1983; Carr et al. 1986). As we've pointed out, the potential repository is located in a layer of densely-welded devitrified tuff. Between the repository and the water table, several stratigraphic intervals containing zeolitic tuffs (containing primarily the zeolites clinoptilolite and mordenite) provide probable barriers to downward radionuclide migration in the unsaturated zone. Additional zeolitic tuffs below the water table provide potential barriers to lateral
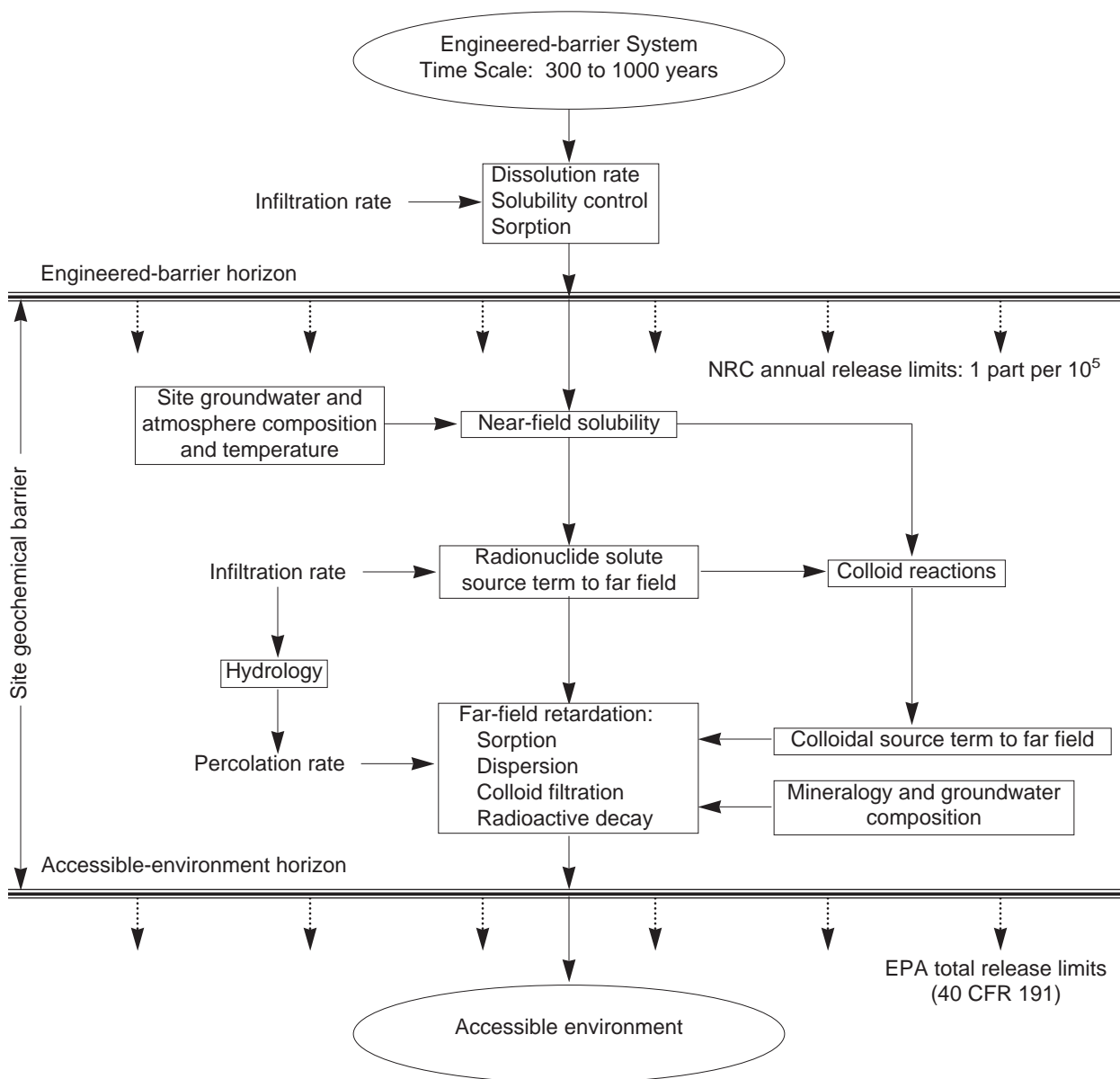
**Figure 2. Multiple Natural Geochemical Barriers.** This schematic diagram of the potential nuclear-waste repository system illustrates the processes important to retardation of radionuclides between the horizon of the engineered-barrier system, where the release limits are stipulated by the NRC, and the horizon of the accessible environment, where release limits are governed by the EPA. For our purposes, the engineered-barrier system is considered independent of the natural site surrounding that system. Taking the NRC limits as the upper bound for releases across the horizon into the natural site, the various processes (sorption, dispersion, colloid reactions, and so forth) are then examined to see if retardation is adequate to meet the EPA release limits to the accessible environment.
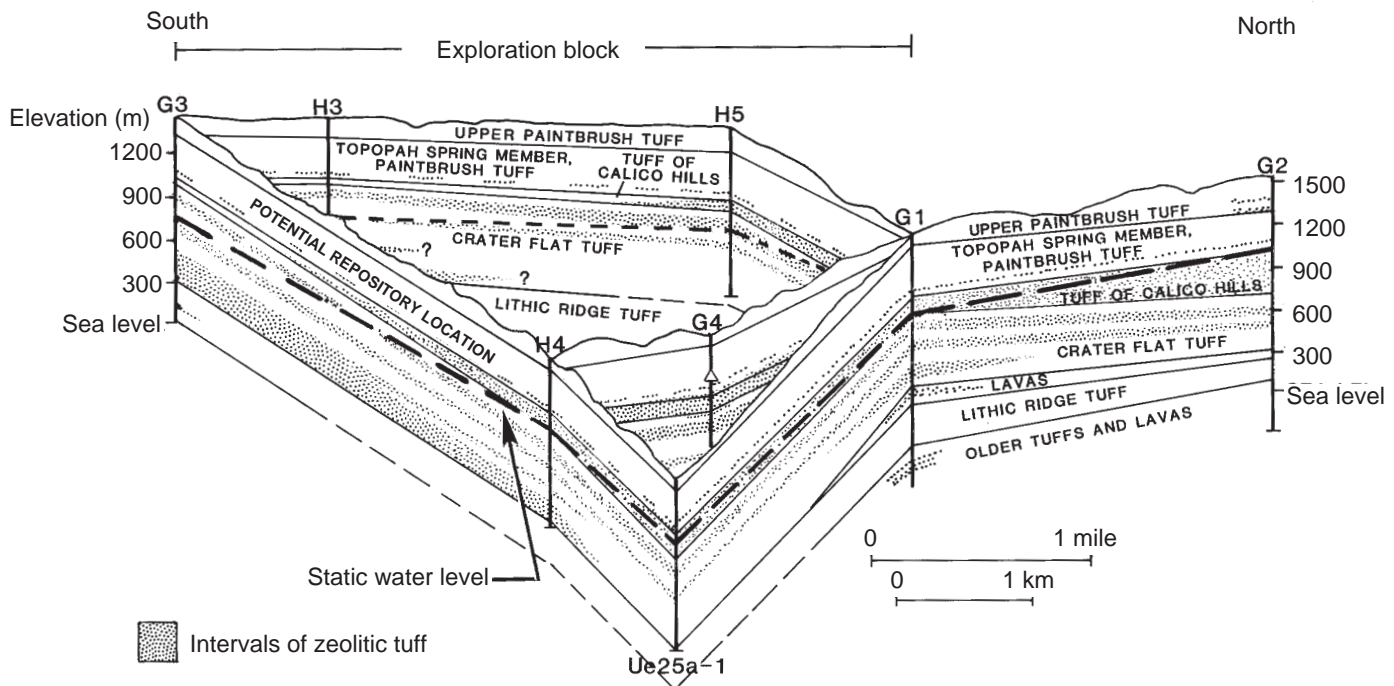
**Figure 3. Zeolitic Tuffs at Yucca Mountain.** The above fence diagram of the stratigraphy at Yucca Mountain shows the distribution of the principal zeolitic tuffs (tuff containing more than 10% clinoptilolite and mordenite) as shaded areas. The potential repository location is in the lower half of the Topopah Spring member of Paintbrush Tuff. Each "fence post" (for example, G3) represents a USW drill hole. Most of the tuff samples used in the research described in this report were portions of core taken from USW drill holes G-1, G-2, G-4, and GU-3 (located at the G3 site). The figure was taken from Broxton et al. (1986); stratigraphic contacts were from Spengler et al. (1979, 1981), Maldonado and Koether (1983), and Scott and Castellanos (1984); preliminary stratigraphic contacts for drill holes USW H-3, H-4, H-5, and G-4 were provided by R. W. Spengler (personal communication, 1983); and static water-level data were from the USGS Nuclear Hydrology Group.

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radionuclide migration through the saturated zone.

The suite of minerals found in the deeper-lying host rock for the potential site includes all four categories of sorptive minerals described by Kent et al. (1988) in the context of a surface-complexation model for radionuclide sorption. These categories are 1) oxide minerals (including iron oxides and silica minerals), 2) multiple-site-type minerals (including the feldspars), 3) fixed-charge minerals (including micas, clays, manganese oxides, and zeolites), and 4) salt-type minerals (including calcite). Chemical speciation and water chemistry may strongly affect the interaction between selected radionuclides and each of these mineral categories, but the mineral variability and presence of all four mineralogic categories of Kent et al. suggest mineralogic robustness for sorption at Yucca Mountain.

Beneath the potential host rock, the stratified layers of devitrified (mostly quartz plus feldspar) and nonwelded (mostly glass or zeolite) tuffs provide significant mineral variability along both unsaturated and saturated transport pathways. The effectiveness of the individual mineral types in sorbing will depend on the geometry, accessibility, fluid environment, duration of contact, and cumulative abundance along the transport pathway.

## B. AN INTEGRATED APPROACH TO SITE CHARACTERIZATION

The natural system at Yucca Mountain defines the site-specific conditions under which we must determine to what extent the natural geochemical barrier will prevent the migration of radionuclides away from the repository. The mineralogy, petrology, and water chemistry at Yucca Mountain define the conditions a radionuclide will encounter if the waste package corrodes and dissolved radionuclides are released across the horizon of the engineered-barrier system into the site environment. There may be many scenarios that could affect the near-field environment, creating chemical conditions more aggressive than conditions presented by the unperturbed system (such as pH changes beyond the range of 6.9 to 8.9 or significant changes in the ionic strength of near-field waters). Without clear near-field-condition bounds at this time, we assume that at some distance away from the waste package, conditions are dominated by the large rock-mass buffer. In the far field, the near-neutral, oxidizing, low-ionic-strength conditions of the normal site environment control the radionuclide solubility limits and the sorption capacity of the tuff.

Our testing strategy (Canepa et al. 1994) thus shows the need for characterization of the natural system, which defines the experimental conditions for solubility and sorption determination. Such characterization requires data on groundwater composition, including natural colloids, on the mineralogy and petrology of the rock, and on mineral stability. Modeling of the groundwater chemistry is designed to lead to an understanding of solubility and speciation of the important radionuclides as well as the possible formation of radiocolloids. Laboratory experiments attempt to characterize sorption and diffusion of the radionuclides in light of this information. Finally, validation of chemical processes in a dynamic system is crucial before laboratory data are applied to the field tests or natural analogs. In this report, we focus on summarizing the research that has been accomplished in the areas described below.

## Modeling of Groundwater Chemistry

The purpose of the groundwater-chemistry modeling task is to develop models that describe compositional variations in groundwaters in the unsaturated and saturated zones beneath Yucca Mountain. These models are used to establish bounds on the water compositions to be expected in the ambient Yucca Mountain flow system. They are also used to bound the composition of waters in the far field of the potential repository at Yucca Mountain in the post-closure period.

We can also derive estimates of the possible range of water compositions to be expected in the Yucca Mountain flow system on the basis of the compositional variations observed in present-day groundwaters in volcanic units over a large area such as the Nevada Test Site. The programs to measure transport parameters, such as sorption coefficients and solubilities, incorporate the compositions of these waters as part of the experimental design.

## Radionuclide Solubility Studies

The potentially limited solubility of radionuclides in groundwater can be thought of as the geochemical first line of defense against migration. Evaluation of this effect first requires a knowledge of the groundwater chemistry at the site and the expected spatial and temporal ranges of its variability. Second, quantitative determinations of radionuclide solubility in groundwater within this range of chemistry must be made. Speciation and molecular complexation must be ascertained to interpret and apply solubility results. The solubilities thus determined can be used to assess the effectiveness of solubility in limiting radionuclide migration. We can also use these solubilities to evaluate the effectiveness of other retardation processes expected to operate once any dissolution and migration begin.

The short-term goals of the radionuclide solubility task have been to provide solubilities from bulk experiments that attempt to bracket our current estimate of groundwater conditions that might

exist. Intermediate goals have been to develop the thermodynamic database for solution speciation and solid-state determination as a prerequisite to modeling the results. Once the model is self-consistent and performs well against known solubilities, our long-term goal is to use the model over a continuous, weighted distribution range of potential groundwaters to generate a weighted distribution of solubilities that could be used for performance assessment of the site.

**Sorption Studies**

A geochemical second line of defense against groundwater transport of radionuclides is "sorption," which comprises several physicochemical processes, including ion exchange, adsorption, and chemisorption. Determining whether sorption will occur requires knowledge of the likely flow paths of the groundwater and the spatial and temporal distribution of sorbing minerals along these paths. Evaluating the retardation effectiveness of sorption for repository design and licensing requires theoretical and quantitative understanding of sorption.

Batch-sorption experiments are useful for bounding more detailed and mechanistic sorption studies. We determined batch-sorption distribution coefficients, defined as

$$K_d = \frac{\text{moles of radionuclide per g of solid phase}}{\text{moles of radionuclide per ml of solution}} \ , \ (1)$$

as a function of variables representing conditions expected beyond the region disturbed by waste emplacement. The variables included mineralogy, groundwater chemistry, sorbing element concentration, atmospheric conditions, and temperature.

Batch-sorption results are very sample specific and, therefore, difficult to generalize and apply throughout the mountain. Deconvolution of sorption isotherms provides much greater detail about sorption sites (kind, number, specificity, and so forth). Such information can be correlated with crystallographic data and related to specific sorption sites in the crystal structure. All sites are not equally selective for all sorbing species. Examining the sorption behavior of individual pure minerals, such as the zeolites and manganese or iron oxyhydroxides found in Yucca Mountain tuffs, could help predict sorption coefficients along flow paths of known mineral content.

One factor that can have an effect on the sorption of radionuclides is organic materials. Naturally occurring organic compounds generated during the transformation of plant and animal debris over time and as a result of the synthetic activities of microorganisms are ubiquitous in surface and subsurface environments. Sorption of organic material onto mineral surfaces can affect the properties of those surfaces, such as charge and hydrophobicity, thereby altering the reactivity of the mineral toward metal ions. A clear understanding of the effects of the organics that frequently coat mineral surfaces in natural environments will lead to improvements in the sorption models used to predict the mobility of radionuclides in natural aquatic environments.

A better understanding of the sorption of radionuclides onto tuff will be possible if we can relate the data to mechanistic models. Two general mechanisms are important: ion-exchange reactions that are primarily electrostatic in nature and surface complexation in which a relatively covalent chemical bond forms with the mineral surface. Ion exchange does not have the same degree of selectivity between aqueous ions of like charge as does surface complexation. The adsorption of metal ions via cation exchange will only occur on surfaces of opposite charge and so is affected by such common components of groundwater as sodium. Surface complexation, on the other hand, can occur even when the mineral surface charge is the same as the aqueous ion. Both of these processes can, in principle, be modeled using a triple-layer surface-complexation model. However, there are significant differences between the cation exchange in zeolites and clays and the formation of surface complexes on metal oxides, so we have treated cation exchange and surface complexation separately.

Physiochemical processes that might accelerate radionuclide migration relative to groundwater flow rates, such as anion exclusion, must also be quantified. These depend largely on the molecular complexation or speciation that occurs in solution. Accordingly, detailed assessment of this possibility is needed to fully evaluate the potential for transport retardation by geochemical processes.

### Diffusion Studies

Additional geochemical lines of defense beyond solubility limits and sorption are possible. The lateral diffusion of radionuclide species in porous media may retard longitudinal migration by bringing dissolved radionuclides into contact with sorbing minerals. Also, when the fluid flow is through fractures in highly impermeable rock and there is an absence of sorbing minerals on the fracture surfaces, diffusion may be the only effective retardation mechanism. Most rock (even dense rock such as granite) has small fissures between the crystals that interconnect the pore system containing water. Small molecules of radioactive materials can diffuse in and out of this pore system. The inner surfaces in the rock matrix are much larger than the surfaces in the fractures on which the water flows, and the volume of water in the microfissures is much larger than the volume in fractures. Therefore, over a long time scale, diffusion can play an important role in radionuclide retardation.

Diffusion experiments can provide diffusion information on nonsorbing neutral molecules and anions and on sorbing radionuclides. And because diffusion experiments measure the uptake of radionuclides by tuff as a function of time, information is gained on the kinetics of sorption. The work described here is of two types. In rock-beaker experiments, we placed a radionuclide solution inside the rock beaker and measured the decrease in radionuclide concentration as a function of time. In diffusion-cell experiments, a slab of tuff separates two chambers of groundwater, and we measured the concentration of radionuclide diffusing across the slab from one chamber to the other as a

function of time.

### Dynamic Transport Studies

Sorption results also must be interpretable and applicable to dynamic and heterogeneous systems, so we developed diffusion and dynamic transport experiments to complement and extend the batch-sorption results to such systems. Three types of dynamic transport experiments were conducted: crushed-rock column experiments, whole-rock column experiments, and transport through fractures.

We used crushed-rock experiments to study kinetic phenomena affecting sorption, including ionic and molecular diffusion. Whole-rock experiments additionally illustrate advective dispersion effects. Fractured-rock experiments represent the closest laboratory approach to the actual environment in which fluid flow and radionuclide migration might occur in an unanticipated scenario.

Studies are also necessary to determine the transport of radionuclides along fractures passing through the site. In the candidate host rock, the fractures contain a complex development of cristobalite, zeolites (mostly clinoptilolite and mordenite), manganese minerals, and calcite (Kent et al. 1988). This composition is in marked contrast to the rock matrix, composed predominantly of feldspars and silica minerals (quartz, cristobalite, and tridymite). Thus, different mechanisms are likely for retardation of radionuclides in flow along fractures and flow through bulk rock, and we have studied these mechanisms using fractured-rock columns.

The fracture-column studies also afforded us an opportunity to investigate colloidal radionuclide migration. Colloidal species may escape sorption and be too large to diffuse, that is, simple filtration may operate to retard movement. On the other hand, fracture flow may afford an easy transport path for colloids to the accessible environment. The dynamic transport experiment is a difficult but powerful method for elucidating separate and coupled processes affecting radionuclide migration.

We also evaluated the likelihood of particle or colloid formation by analyzing a typical Yucca Mountain groundwater for the presence of natural colloids and by conducting laboratory experiments to determine the possibility of radiocolloid formation. We estimated the rate of particle aggregation for various colloids using autocorrelation photon spectroscopy.

The use of batch-sorption experiments to identify sorption mechanisms and to obtain sorption distribution coefficients is fast, easy, and inexpensive compared to other types of sorption experiments. However, measurements made under flowing conditions must be carried out to verify the results of the static batch-sorption experiments. We performed such verification using crushed-tuff and solid-rock column experiments in which mass-transfer kinetics were investigated by measuring radionuclide migration as a function of water velocity. The differences between the column and the batch-sorption experiments should be sensitive to multiple-species formation, colloid formation, and other geochemical reactions not adequately described by batch-sorption coefficients.

## Quality Approved Detailed Procedures

All work performed to collect data and test, analyze, model, or describe the natural system under study has been done under the Yucca Mountain Project Quality Assurance program at Los Alamos. In particular, all experimental procedures were carried out in conformance with quality-approved procedures that are described in the *Yucca Mountain Project Detailed Procedures* at Los Alamos. The various procedures for each experimental area and the corresponding reference for the current version of that procedure are listed in Table 2.

### The Reference Information Base

The stratigraphy referenced in this report is consistent with the Yucca Mountain Project Reference Information Base Section 1.12(a), "Stratigraphy: Geologic/Lithologic Stratigraphy" and with the Prototype Three-Dimensional Framework Model of September, 1995.

**Table 2.  Los Alamos Yucca Mountain Project Detailed Procedures**

| Research area | Procedure | Reference number |
|---|---|---|
| General | pH measurement | LANL-CST-DP-35 |
| | Rock sample preparation (crushing and sieving) | LANL-CST-DP-63 |
| | Neptunium, plutonium, and americium solution preparation | LANL-CST-DP-78 |
| | Liquid-scintillation counting | LANL-CST-DP-79 |
| | Eh measurement | LANL-CST-DP-102 |
| Diffusion | Saturated diffusion-cell experiments | LANL-CST-DP-66 |
| | Rock beaker experiments | LANL-CST-DP-67 |
| Sorption | Batch sorption under atmospheric conditions | LANL-CST-DP-86 |
| | Batch sorption within controlled atmosphere of a glove box | LANL-CST-DP-100 |
| Colloids | Particle size distribution (autocorrelation photon spectroscopy) | LANL-CST-DP-75 |
| | Colloid sampling | LANL-CST-DP-101 |
| Dynamic transport | Crushed-rock column studies | LANL-INC-DP-15 |
| | Solid-rock column experiments | LANL-INC-DP-61 |
| | Fracture core experiments | LANL-INC-DP-68 |

### C. YUCCA MOUNTAIN WATERS

A strategy for determining the retardation of radionuclides must be compatible with the hydrology of the site. A generalized conceptual model of unsaturated-zone water flow in Yucca Mountain is shown in Fig. 4 (Montazer and Wilson 1984). According to Montazer and Wilson, water in the unsaturated portion of this system will flow dominantly in the matrix and intermittently in the fractures. Given the low infiltration rate at Yucca Mountain, the rate of water movement in the matrix should be slow (Sinnock et al. 1984), but according to the modeling efforts of Nitao and Buscheck (1989), the rate of water movement in the fractures may actually be fairly rapid. The question of whether or not there will be significant water flow in the fractures beneath the potential repository horizon after waste has been stored

there is unresolved at the present time.

### Saturated-zone Groundwater Chemistry

The chemical compositions of groundwaters in the present and future groundwater flow systems are important parameters with regard to the sorption behavior of important radionuclides in this system. Our chemistry and transport studies used water from the Yucca Mountain region, particularly from Well J-13, which accesses the water table several miles east of Yucca Mountain. The uplifted block of tuff units that make up Yucca Mountain dips to the east, and at the J-13 location, the water table and the Topopah Spring Member intersect. Water from Well J-13, although not exactly representative of Yucca Mountain unsaturated pore water, has been in contact with the same unit proposed for the repository and can be used as a reference water.
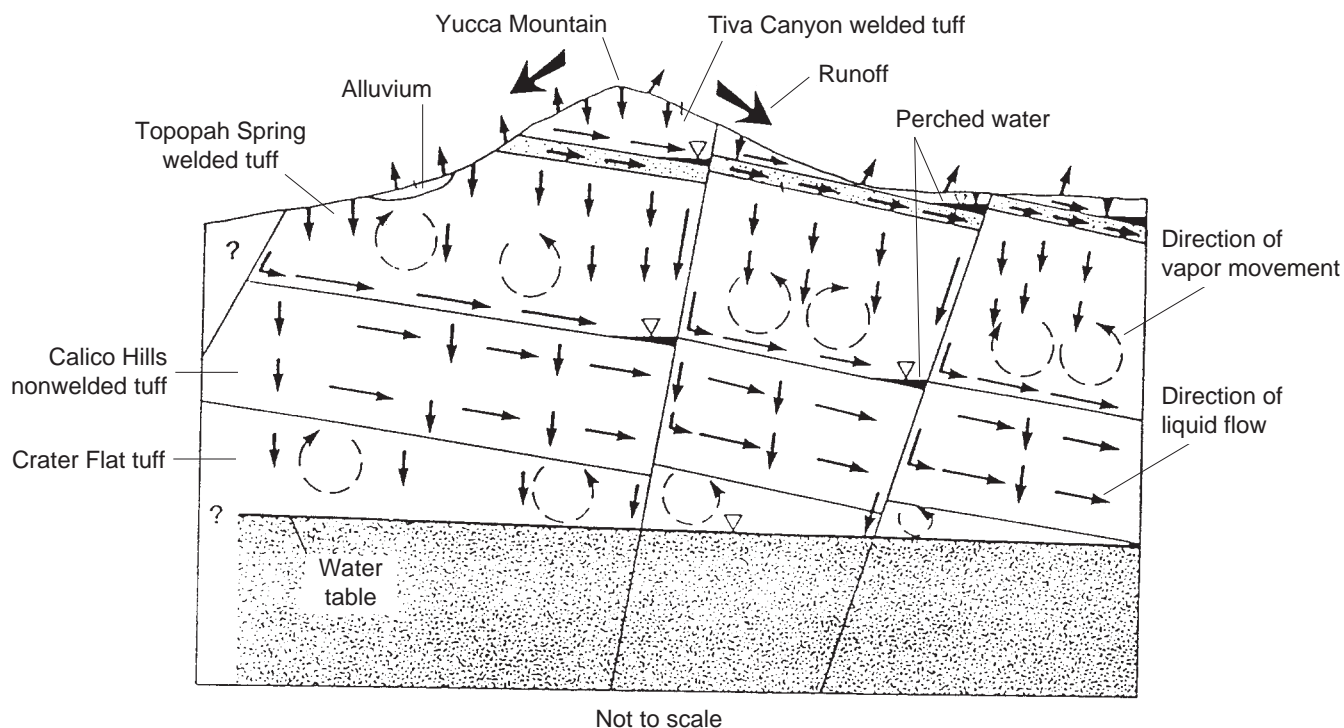


**Figure 4. Unsaturated-zone Hydrology Model.** This generalized east-west section across Yucca Mountain shows the flow regime under baseline conditions. Dashed arrows indicate movement of water vapor; solid arrows indicate movement of liquid water; and the lengths of the arrows indicate relative magnitude of the fluxes (from Montazer and Wilson 1984).

**J-13 Well construction**

Details of the construction and penetration levels of Well J-13, located in Fortymile Wash, are presented in Fig. 5. The total depth of the well is 3,500 feet, and it has been producing since its completion in 1963. Inspection of the construction diagram reveals perforations from a long section below the Topopah Spring Member starting at 2,690 feet. However, because of a discrepancy in the records concerning the well configuration (Harrar et al. 1990), it is not clear whether the entire length of the 5.5-inch liner below 1,499 feet is slotted or whether only the interval shown in the figure below 2,690 ft. is open. Resolving this discrepancy is not very important because there is no cement behind the liner, thus providing access to the well to any fluids entering the borehole below about 1,550 feet. However, hydraulic tests performed on the well yielded transmissivities that indicated that only about 20% of the flow may come from other formations, such as the tuffaceous beds of Tuff of Calico Hills, the three Crater Flat Tuff members, and Tuff of Lithic Ridge.

**Well UE-25 p#1**

Another well, Well UE-25 p#1, is located roughly midway between Yucca Mountain and Well J-13 at a ground-level elevation about 100 meters higher than Well J-13. Water from this well is drawn from the deep paleocarbonates underlying the tuff sequences. It has been the only other water available from the Yucca Mountain region with a chemistry different from J-13 water.

The data available in 1984 on the chemistry of saturated-zone groundwaters were reviewed by Ogard and Kerrisk (1984). In the volcanic units, the groundwaters are basically dilute sodium-bicarbonate waters (Table 3). Listed in order of decreasing concentration in J-13 water, the other major cations are calcium, potassium, and magnesium and the other anions are sulfate, nitrate, chloride, and fluoride. The only other major constituent is silica. The water from the Paleozoic aquifer (Well UE-25 p#l) has higher concentrations of almost all these constituents. Thus, the ionic strength of Well

UE-25 p#1 water is higher than that of J-13 water, although both are relatively low in ionic strength.

The chemistry of groundwaters from Wells J-13 and UE-25 p#1 seems to bound that of the Yucca Mountain groundwaters (Meijer 1992), and thus, these two groundwaters serve as standards for the experimental work. However, certain changes (Fig. 6) take place in the chemistry of the waters between their removal at the well and their use in the laboratory. The J-13 and UE-25 p#1 reference data plotted in Fig. 6 was obtained on site by Ogard and Kerrisk (1984). This on-site chemistry is compared with the chemistry of aliquots of J-13 and UE-25 p#1 waters that were collected at later dates, sent to Los Alamos, and filtered. On site, the pH of the two groundwaters is ~7. However, at Los Alamos, the waters equilibrate in the higher-elevation atmosphere with subsequent evolution of carbon dioxide, which causes the pH of J-13 water to increase to 8.5 and the pH of UE-25 p#1 water to increase to ~9. The data of Fig. 6 indicate that

**Table 3. Chemistry of Waters from Wells J-13 and UE-25 p#1 and the Unsaturated Zone (UZ) at the Yucca Mountain Site**

| Element | J-13*<br>(mg/l) | UZ**<br>(mg/l) | UE-25 p#1*<br>(mg/l) |
|---|---|---|---|
| Sodium | 45 | 26–70 | 171 |
| Bicarbonate | 143 | — | 698 |
| Calcium | 11.5 | 27–127 | 87.8 |
| Potassium | 5.3 | 5–16 | 13.4 |
| Magnesium | 1.8 | 5–21 | 31.9 |
| Sulfate | 18.1 | 39–174 | 129 |
| Nitrate | 10.1 | — | < 01 |
| Chloride | 6.4 | 34–106 | 37.0 |
| Fluoride | 2.1 | — | 3.5 |
| Silicon | 30.0 | 72–100 | 30.0 |
| | | | |
| pH | 6.9 | 6.5–7.5 | 6.7 |
| Eh (mV) | 340 | — | 360 |

*Ogard and Kerrisk 1984; **Yang et al. 1990.

Casing diameter
(cm)

**45.7**
**34.0**
**20.8**
**14**

Depth below land surface
(m)          (ft)

| Stratigraphic unit | Major lithography |
|---|---|

Alluvium — Sand and gravel

Tiva Canyon Member — Ash-flow tuff, partly welded and partly zeolitized

132.5    435

207.3    680

Topopah Spring Member — Ash flow tuff, welded, lithophysae common

Paintbrush Tuff

449.6    1475

Tuff of Calico Hills — Bedded and reworked tuff, zeolitized

530.4    1740

Prow Pass Member — Ash-flow tuff, partly welded and partly zeolitized

596.2    1956

Bullfrog Member — Ash-flow tuff, partly welded, zeolitized, and clayey

707.1    2320

Crater Flat Tuff

← Section that may not be perforated

5.5-inch liner →

Tram Unit — Ash-flow tuff, partly welded and partly zeolitized

← Section with known perforations

975.4    3200

Lithic Ridge Tuff — Ash-flow tuff, argillized and zeolitized
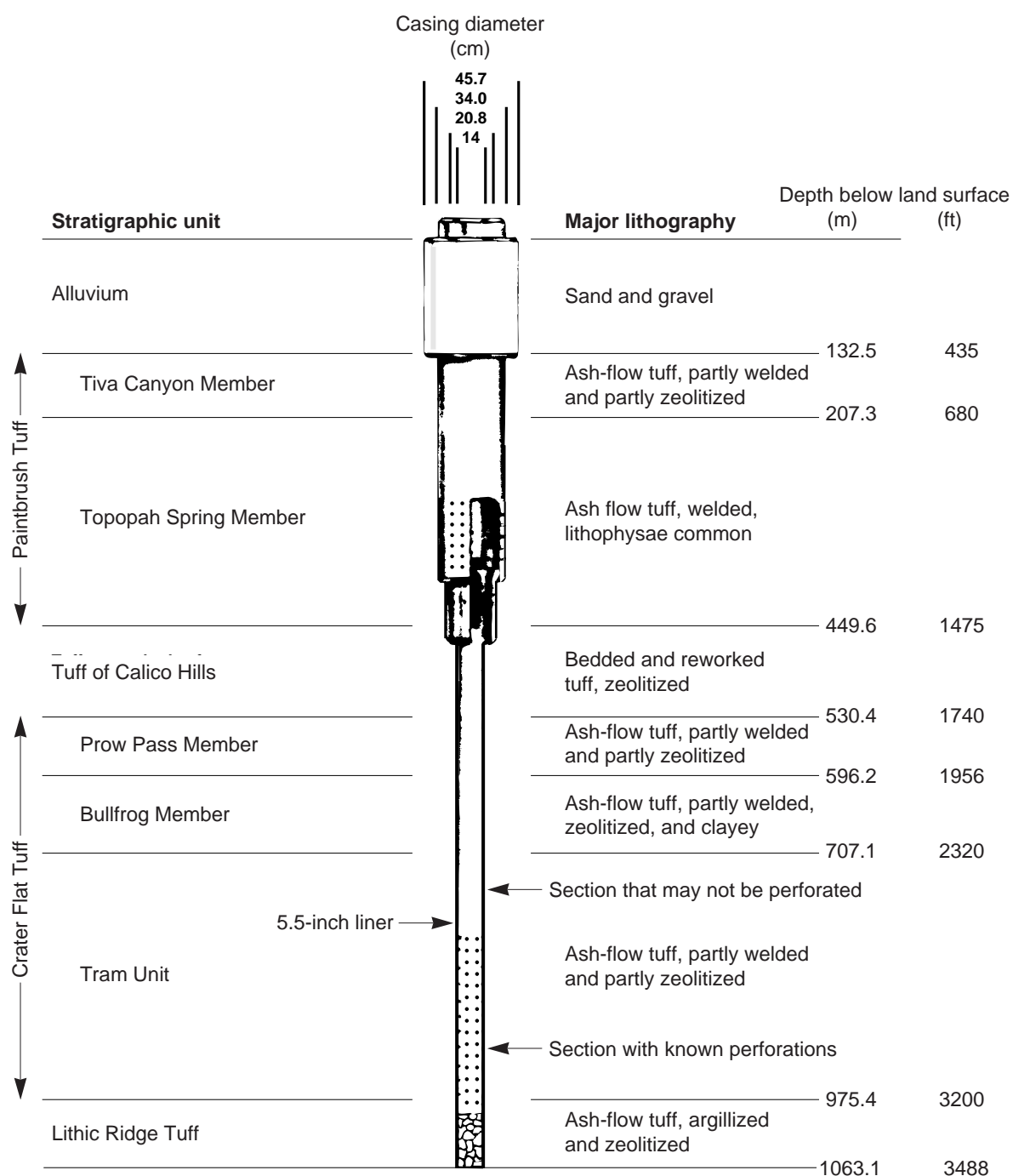
1063.1    3488

**Figure 5.  Well J-13.**  The construction diagram and lithologic units penetrated for Well J-13 (from Harrar et al. 1990) are shown above.  Hydraulic tests performed on the well indicate that about 80% of the water flow may come from the Topopah Spring Member of Paintbrush Tuff, which is the same stratigraphic unit as the one proposed for the repository, and only about 20% may come from other formations.
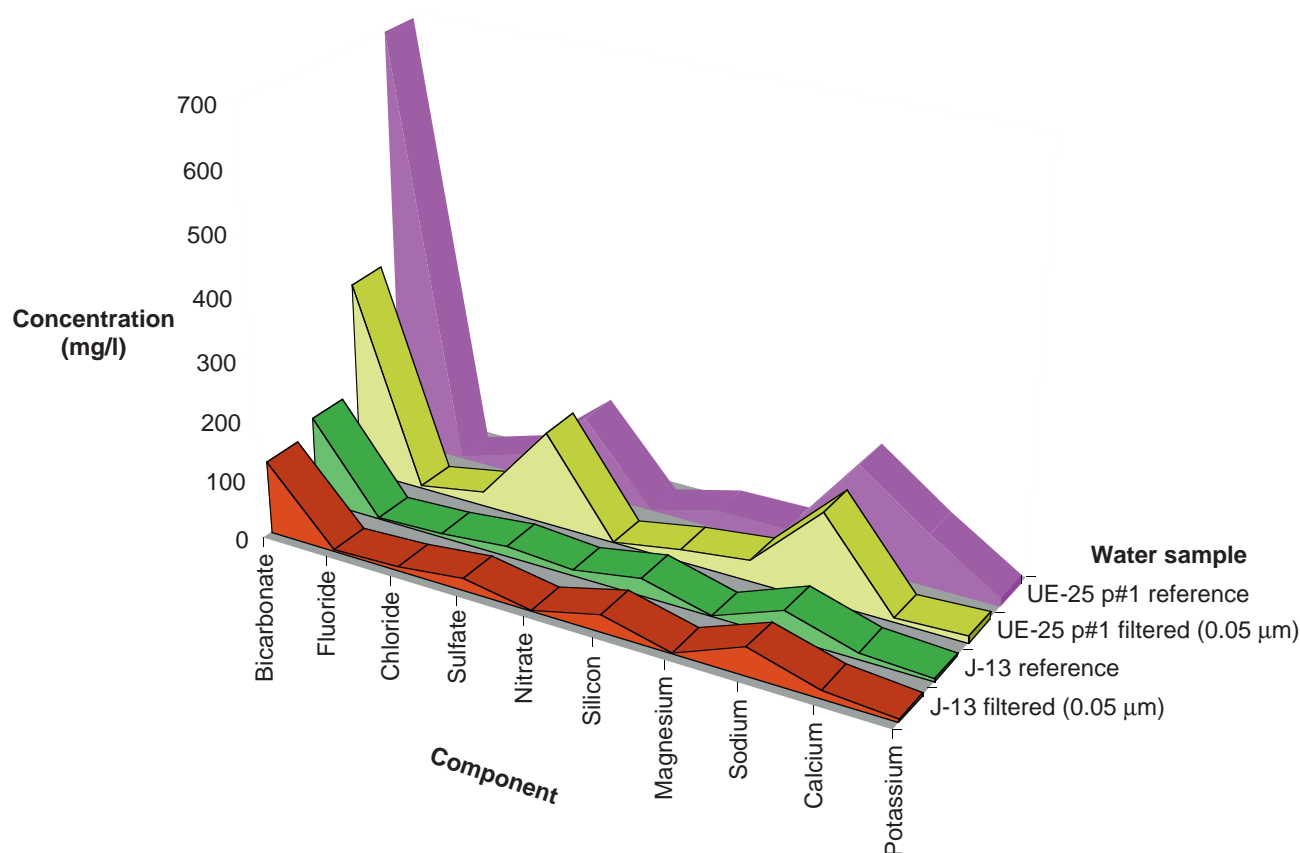
**Figure 6. Chemistry of Two Groundwaters.** The two reference samples above are water analyzed on-site in Nevada at the J-13 and UE-25 p#1 well sites (Ogard and Kerrisk 1984). The filtered samples are water analyzed at Los Alamos, NM, after being passed through a 0.05-$\mu$m filter (data recorded in binder TWS-INC-11-93-32, pages E24–E25, for J-13 water and in binder TWS-INC-03-93-02, page C8, for UE-25 p#1 water). The figure demonstrates the higher ionic strength of UE-25 p#1 water, the stability of J-13 water, and the apparent calcite precipitation in UE-25 p#1 water caused by $CO_2$ evolution.

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carbon-dioxide evolution and filtration does not otherwise change the chemistry of J-13 water but causes calcite precipitation in UE-25 p#1 water. Consequently, the concentrations of bicarbonate and calcium in any UE-25 p#1 water used in the sorption experiments were lower than that of on-site UE-25 p#1 water. Because both waters are oxidizing, all the sorption experiments were performed under oxidizing conditions.

**Chemical stability of Well J-13 water**
Figure 7 shows a chemical analysis of water from Well J-13 from 1963 to 1993. The front curve represents the average of the chemical analysis of 19 water samples collected between 1963 and 1987 by

five different organizations (Los Alamos National Laboratory, U.S. Geological Survey, Lawrence Livermore National Laboratory, Argonne National Laboratory, and Westinghouse-Hanford Company). Analysis of these results led Harrar et al. (1990) to conclude that the water chemistry of Well J-13 did not change between 1963 and 1987. Comparison of the results of Harrar for that period with similar analyses of water collected in 1992 and 1993 (the other curves shown in Fig. 7) indicates that the chemistry of the water in Well J-13 has been stable for thirty years.

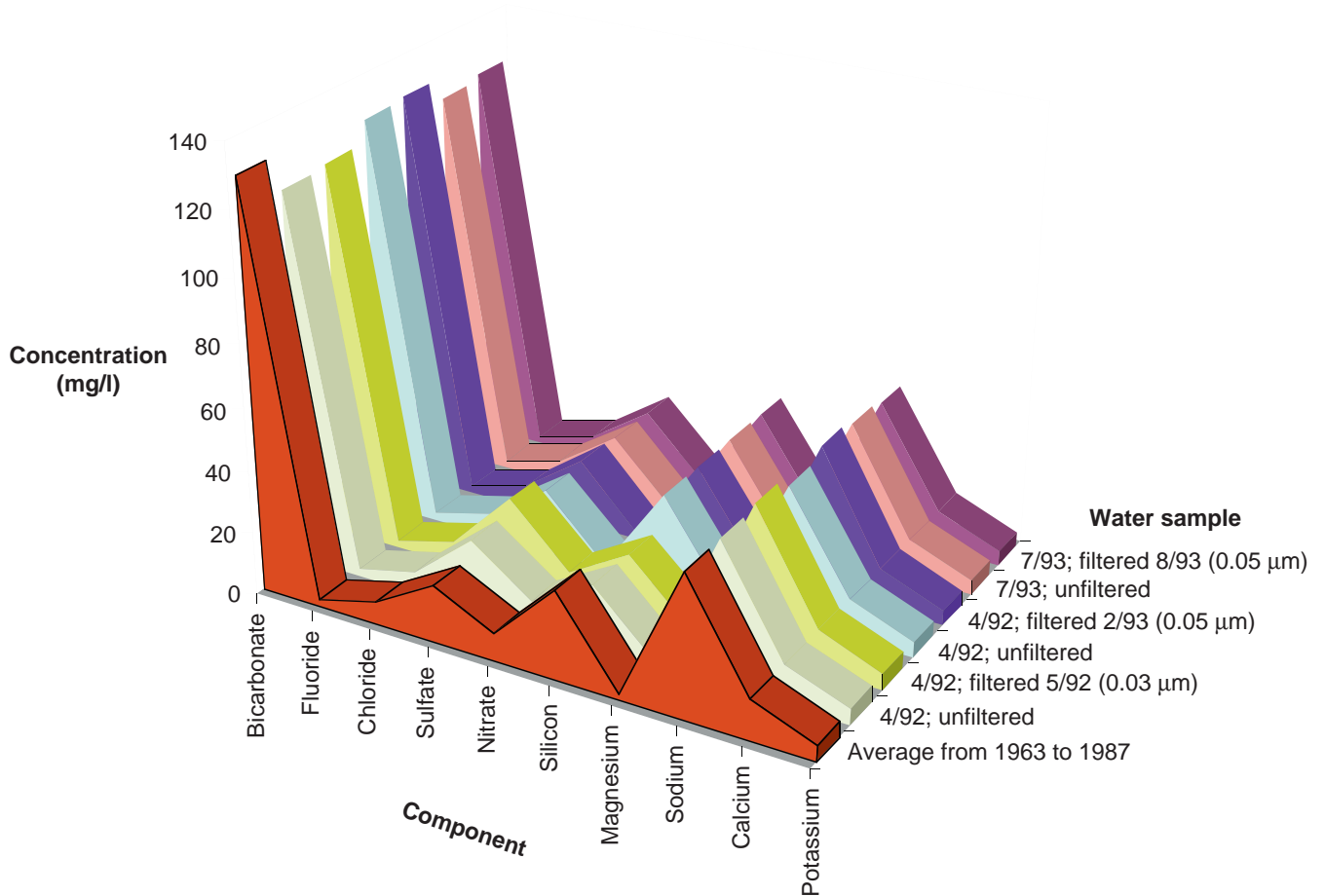We analyzed aliquots of both groundwaters before and after filtration (Figs. 6 and 7). Comparison of

14

**Figure 7. Stability of the Chemistry of Well J-13 Water.** The curves above show minimal compositional changes as a function of collection date, filtering, and filter size, indicating that the chemistry of the water in Well J-13 has been stable for 30 years.

these results indicates that filtration does not cause compositional changes (except for the previously noted calcite precipitation in the UE-25 p#1 water that is caused by pH changes).

**Unsaturated-zone Water Chemistry**

The compositions of waters from the unsaturated zone are not well known. Yang et al. (1990) have reported partial analyses of unsaturated-zone waters from Wells UZ-4 and UZ-5 obtained by tri-axial compression and centrifugation methods. Core samples of the wells from which waters were obtained came from the nonwelded portion of the Yucca Mountain and Pah Canyon members of

Paintbrush Tuff. The major cation and anion concentrations in these waters are intermediate between the saturated-zone tuffaceous waters and waters from the carbonate aquifer (Table 3). Water samples from UZ-4 cores tend to be closer in composition to the tuffaceous waters, whereas waters from UZ-5 cores appear to be closer in composition to water from the carbonate aquifer, although this statement is not intended to imply genetic associations of the waters with these aquifers.

The pH and the oxidizing potential, Eh, of the groundwaters in Yucca Mountain are particularly important with respect to the solubilities and sorption behavior of a number of the important ele-

15

ments (such as, actinides and technetium). The available data suggest that most of the waters within Yucca Mountain site are oxidizing (for example, Ogard and Kerrisk 1984). Because the spatial and temporal variability in the Eh parameter will be difficult to quantify, the conservative approach would be to assume all the groundwaters between the potential repository and the accessible environment are in equilibrium with atmospheric oxygen. This assumption is conservative because all the important (radionuclide) elements have either higher or equal solubilities in oxidizing waters compared with reducing waters. Available data on the pH of waters in Yucca Mountain show a range from 6.5 to 9.4 (Ogard and Kerrisk 1984; Yang et al. 1990). In this case, no single value can be chosen as being conservative.

The future compositional variations of groundwaters in Yucca Mountain must also be considered in the development of a sorption strategy. To a first approximation, the variations are likely to be similar to the present-day variations as a result of buffering reactions by the country rock.

**Pore Water versus Saturated Groundwaters**

We must recognize that there are likely more than one type of water in the Yucca Mountain area. Differences in chemistry may exist between waters in saturated zones (at or below the true water table), waters in tuff pores in the hydrologic units of the unsaturated zone, and perched waters, that is, groundwater separated from the underlying water table by an unsaturated zone.

Unsaturated-zone waters may be strongly influenced by soil-zone processes, including evapotranspiration and the precipitation of pedogenic minerals such as calcite, gypsum, and silica. Chemical properties, such as ionic strength, may be a function of the time interval between infiltration events. Other properties, such as pH and oxidation potential, will depend on the partial pressures in the unsaturated zone of such gases as carbon dioxide and oxygen. Whether or not a particular unit of

rock is closed or open to the gas phases of the unsaturated zone is thus important. Also, the various waters may be influenced by hydrolysis reactions, for instance, with aluminosilicates, or by ion-exchange reactions with zeolites.

Evaluation of the database on water compositions in volcanic units at the Nevada Test Site indicates that the variability in major constituents is well-bounded by waters from Wells J-13 and UE-25 p#1. The main parameters not bounded by these water compositions are pH, Eh, and chloride concentration. Our experimental programs to measure transport parameters, such as sorption coefficients and solubilities, have incorporated these water compositions as part of the experimental design, and we have carried out the experiments as a function of pH. Therefore, the primary uncertainties are in the effects of variations in Eh and chloride concentrations.

**Synthetic Groundwaters**

We used both groundwaters (filtered by a 0.05-$\mu$m filter) in the batch-sorption experiments, but in the column-transport and the diffusion experiments, we used filtered J-13 water and, because of the unavailability of water at that time from Well UE-25 p#1, a sodium-bicarbonate buffer that simulated this groundwater. In the fracture studies, filtered J-13 water and sodium-bicarbonate waters simulating both J-13 and UE-25 p#1 waters were used. One reason for using synthetic waters for the fracture studies was the prevention of microbial activity in the fracture columns.

Synthetic UE-25 p#1 water was prepared by dissolving 0.39 g of $Na_2CO_3$ and 8.90 g of $NaHCO_3$ in 10 liters of deionized water, which duplicates the larger amount of bicarbonate in reference, or on-site, UE-25 p#1 water. Synthetic J-13 water was prepared by dissolving 0.03 g of $Na_2CO_3$ and 1.92 g of $NaHCO_3$ in 10 liters of deionized water.

## D. YUCCA MOUNTAIN TUFFS

The stratigraphy of Yucca Mountain considered from the repository horizon to the accessible environment (and including the repository containers themselves) is outlined in Table 4, which shows the rock type for each of the various strata. We have assumed that, for the purposes of sorption measurements, all strata of the same rock type can be grouped. This assumption reduces the number of sorption coefficient distributions needed to four per radionuclide: iron oxides, devitrified tuff, vitric tuff, and zeolitic tuff. The basis for this grouping is the fact that sorption of radionuclides is the result of a chemical reaction between the radionuclide in the groundwater and the minerals in the tuff. The mineralogy of the different strata of the same type of rock is very similar. Thus, the sorption coefficients can be grouped in terms of these rock types (Thomas 1987).

The repository containers are included on the list because the corrosion by-products of the massive multipurpose containers could become a substrate for sorption. In particular, actinides are sorbed strongly by iron oxides, so iron oxides are given as one of the four "rock" types.

### Mineralogy Variability

The mineralogy and textures of Yucca Mountain tuffs are important to the sorption behavior of the important radionuclides because they determine 1) the types (that is, structure and composition) of mineral surfaces available in the tuffs and 2) the areas of the different mineral surfaces (internal and external) available for sorption of radionuclides.

The mineral species that have been identified in the matrix of Yucca Mountain tuffs are listed in Table 5 in order of overall abundance. Feldspar and quartz are by far the most common matrix minerals (Bish and Vaniman 1985). They are most abundant in the devitrified tuffs, such as those found in the Topopah Spring Member of Paint-brush Tuff, Prow Pass and Tram Members of

Crater Flat Tuff, and the older tuffs.

The zeolites clinoptilolite and mordenite are abundant in parts of some nonwelded units (for example, Calico Hills) but are limited to sparse fracture-lining minerals in most of the devitrified tuffs (see below). In the nonwelded units, the zeolitic zones are thickest in the northern and eastern portions of Yucca Mountain but thin out to the south and west (Bish and Vaniman 1985).

Clays are locally abundant in the matrix of some tuffs (for example, in some parts of the vitrophyres in drill hole G2 and in the bottom of drill hole G1) but are a minor component (1–3%) in most of the tuffs beneath the potential repository (Chipera and Bish 1989).

Calcite is generally a minor component in the tuffs with a bimodal distribution. In most holes, it is a minor-to-abundant constituent at depths less than 300 m and at depths greater than 900 m but is sparse or absent at intermediate depths. Hematite is widely distributed as a trace mineral, particularly in the matrix of the devitrified units.

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### Table 4. Stratigraphy versus Rock Type

| Stratum name | Rock type |
|---|---|
| Repository Container | Iron oxides |
| Repository: Topapah Spring (welded) | Devitrified |
| Vitrophyre below repository: Topopah Spring (welded, vitrophyre) | Vitric |
| Calico Hills (nonwelded, vitrophyre) | Vitric |
| Calico Hills (nonwelded, zeolitized) | Zeolitic |
| Prow Pass (welded) | Devitrified |
| Bullfrog (nonwelded) | Zeolitic |
| Bullfrog (welded) | Devitrified |

**Tuff sample identification**

The tuff samples we used in the batch-sorption and column-transport experiments were obtained from drill holes at Yucca Mountain and labeled with the drill-hole code and drill depth in feet. For example, G4-270 refers to a tuff sample taken from drill hole USW G-4 at a depth of 270 feet. The locations of the drill holes has previously been reported by Bish and Chipera (1989).

The mineralogy of the tuffs that we used in the sorption, diffusion, and transport experiments was determined by x-ray-diffraction (XRD) analysis (Fig. 8), the details of which were previously reported (Bish and Chipera 1989; Chipera and Bish 1989, 1994). Prior to their use in the sorption and the crushed-rock-column experiments, all tuff samples were crushed and wet-sieved (with the groundwater being used in the experiment) to obtain particle sizes ranging from 75 to 500 μm. As previously discussed by Triay et al. (1996a), such crushing and sieving does not cause significant differences in the mineralogy of the tuff samples. In several cases, it appears that sieving to eliminate particles smaller that 75 μm reduces the smectite content. Because smectite is a good sor-

ber for most radionuclides, the sieved tuff samples should yield conservative results for the sorption measurements.

For our experiments, we always used several examples of each of three major rock types for tuff: zeolitic, vitric, and devitrified. Each of these are now briefly described.

**Zeolitic tuff**

The zeolitic tuffs are represented in Fig. 8 by samples G4-1508 and G4-1510. The major component of these tuffs is clinoptilolite. Other components usually include opal-CT, quartz, and feldspar.

**Vitric tuff**

The vitric tuffs are represented in Fig. 8 by samples GU3-1405 and GU3-1407. The major component of the vitric tuffs is glass. Another component is usually feldspar. Sample G2-723 is another vitric tuff, but this sample also has a significant component of calcite.

**Devitrified tuff**

The devitrified tuffs are represented in Fig. 8 by samples G4-268 and G4-270. The major component of the devitrified tuffs is alkali feldspar. Another component of the devitrified tuffs is usually tridymite.

**Minerals**

In some of the sorption experiments, we used natural and synthetic minerals. The intent was to identify those minerals responsible for dominating radionuclide sorption onto tuff by measuring sorption with single mineral phases. The natural minerals we used were calcite, montmorillonite, bentonite, clinoptilolite (purified with sodium exchange), quartz, and albite. The synthetic minerals we used were calcite and hematite, which were commercially available $CaCO_3$ and $Fe_2O_3$, respectively.

**Surface area of tuffs and minerals**

Originally, the available data on total surface area of tuff samples from Yucca Mountain were rather

### Table 5. Minerals in Matrices of Yucca Mountain Rocks

| Major phases | Minor and trace phases |
|---|---|
| Quartz | Hematite |
| Alkali feldspar | Dolomite |
| Clinoptilolite | Chlorite |
| Cristobalite | Illite |
| Plagioclase | Fluorite |
| Tridymite | Hornblende |
| Opal-CT | Pyroxene |
| Smectite | Fe-Ti Oxides |
| Mica | Ilmenite |
| Mordenite | Zircon |
| Analcime | Allanite |
| Calcite | Sphene |
| (Glass) | Rutile |

limited. Wolfsberg et al. (1979) reported surface areas (via the BET method using nitrogen as the adsorbate) for three samples with a range of values from 2.6 to 10.0 m$^2$/g. Data on the specific surface areas of the various mineral phases in Yucca Mountain tuffs were not available. Wolfsberg and Vaniman (1984) presented a summary of "cation-exchange capacities" for Yucca Mountain tuffs. The zeolite and the clay-rich tuffs had cation-exchange capacities in the range from 10 to 175 meq/l00 g, and the capacities of devitrified and vitric tuffs were in the range from 0.1 to 10 meq/l00 g.

We performed further surface-area measurements on the tuff samples and the minerals using the

BET analysis method. Typical values are shown in Fig. 9.

**Fracture Minerals**

The Yucca Mountain region has undergone significant deformation due to tectonic and volcanic activity. As a result, many faults and fractures were produced within the tuffaceous units as well as the entire region. In addition, volcanic tuffs are often fractured as a result of cooling. The numerous fractures present at Yucca Mountain potentially represent a breach in the natural barrier by providing a fast pathway for contaminant migration.

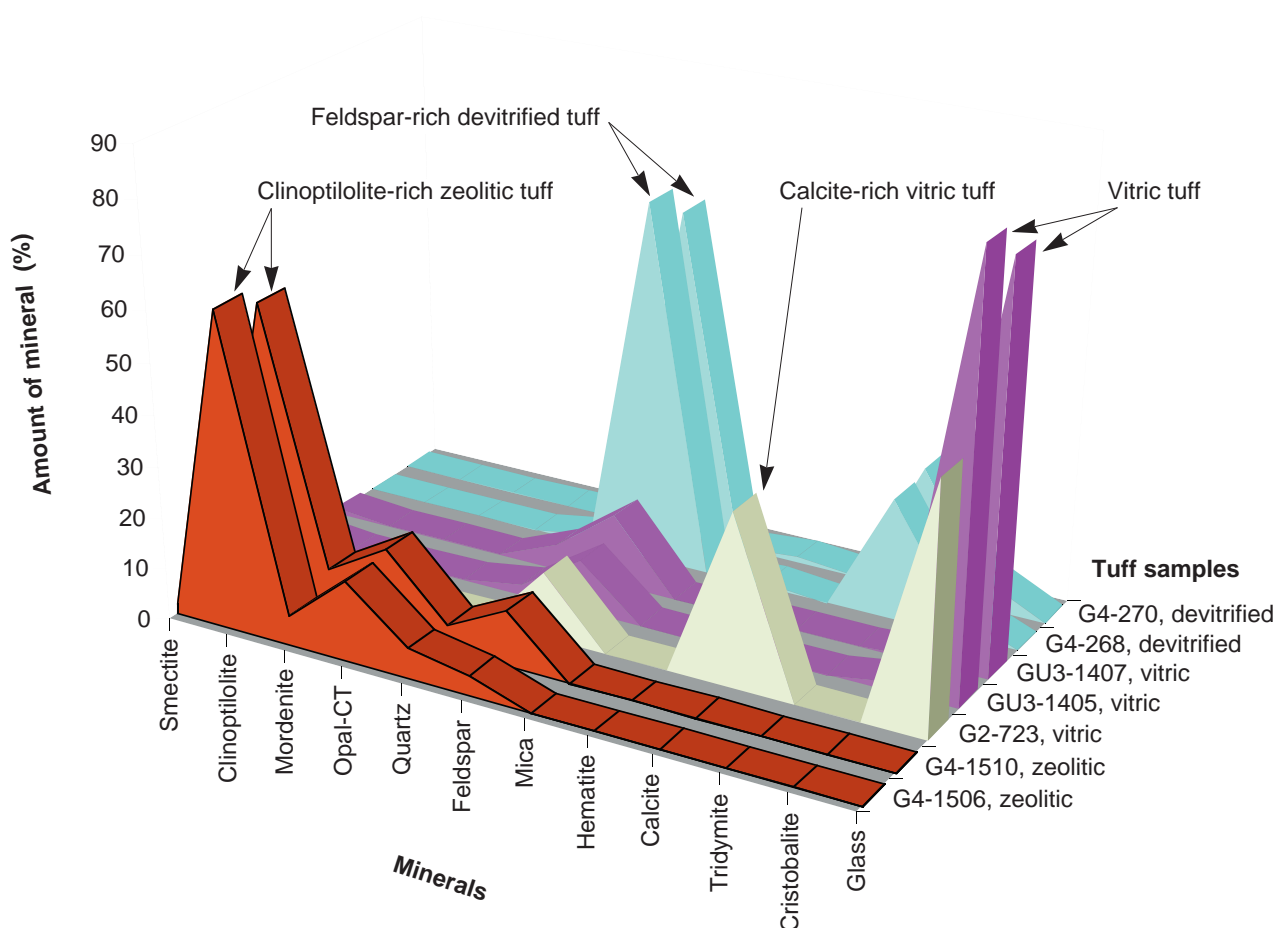Radionuclide transport calculations often assume



**Figure 8. X-ray Diffraction Results.** Mineral percentages determined by x-ray diffraction for tuffs used in the experiments are shown. Each tuff, except GU3-1405, was wet-sieved with J-13 well water to particle sizes ranging from 75 to 500 μm.

that radionuclides can travel through fractures unimpeded. This assumption is too simplistic and leads to overconservative predictions of radionuclide releases to the accessible environment. The assumption ignores two of the main retardation mechanisms: diffusion of the radionuclides from the fractures into the rock matrix and sorption of radionuclides onto the minerals coating those fractures.

Minerals coating the fracture walls are generally different from the host-rock mineralogy due to a variety of factors, such as precipitation of hydrothermal waters or alteration of the pre-existing minerals. The minerals lining the fractures found at the Yucca Mountain site (Carlos 1985, 1987, 1989, 1990, 1994; Carlos et al. 1993) are given in Table 6.

Although a relatively large number of fracture minerals have been identified, the overall abundance of these minerals is very small. Manganese minerals are found in fractures throughout most of the holes for which data are available, except in one drill hole where they are restricted to the upper few hundred feet. In most of the holes for which data

are available, calcite is common in fractures within a few hundred feet from the surface, is minor or absent in the middle sections of the holes, and is again common in fractures in the lower parts of the holes, which is consistent with the abundance variations of calcite in the matrix. Clays and zeolites generally increase in abundance in fractures with depth and are the dominant secondary minerals in the lower parts of some holes. Silica and iron-oxide/oxyhydroxide phases are somewhat unevenly distributed in fractures but are nonetheless important fracture-lining phases.

Data on the concentrations of elements on surface sites on minerals in Yucca Mountain tuffs are very limited at present. The minerals for which the greatest number of data are available are the zeolites and clays. This emphasis exists because measurement of the bulk cation abundances (that is, calcium, magnesium, sodium, and potassium) in these minerals reflects the cation populations on intracrystalline exchange sites accessible to aqueous species.

Broxton et. al. (1986) have tabulated chemical data for zeolites and clays from various volcanic units
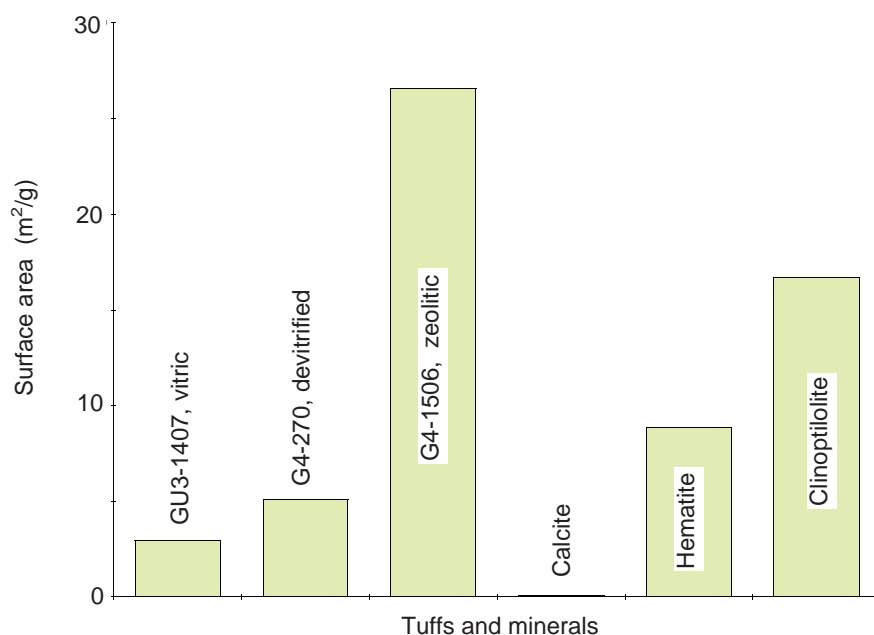


**Figure 9. Surface Areas of Tuffs and Minerals.** BET analysis was used to determine the surface areas of the tuffs and minerals used in the sorption experiments. The tuffs and the calcite (natural) were wet-sieved with J-13 well water to obtain particle sizes ranging from 75 to 500 μm. The hematite (synthetic) and clinoptilolite were not sieved.

**Table 6.  Minerals Coating Fracture Walls in Yucca Mountain Tuffs**

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### Zeolites

| | |
|---|---|
| Heulandite | Chabazite |
| Clinoptilolite | Phillipsite |
| Mordenite | Erionite |
| Analcime | Stellerite |

---

### Silica

| | |
|---|---|
| Quartz | Feldspars |
| Tridymite | Plagioclase-albite |
| Cristobalite | K-feldspar-sanidine |
| Opal | |

---

### Clays

| | |
|---|---|
| Smectites | Sepiolite |
| Montmorillonite | Palygorskite |
| Saponite | Illite |

---

### Manganese-oxides/hydroxides

| | |
|---|---|
| Aurorite | Rancietite |
| Cryptomelane | Romanechite |
| Hollandite | Todorokite |
| Coronadite | Pyrolusite |
| Lithiophorite | |

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### Iron-oxides/hydroxides

| | |
|---|---|
| Hematite | Magnetite |

---

### Carbonates and Halides

| | |
|---|---|
| Calcite | Fluorite |

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in Yucca Mountain.  In general, samples from the west side of the potential repository block are sodium and potassium rich, whereas the eastern samples are enriched in calcium and magnesium (Broxton et al. 1986; Fig. 1).  Carlos (1985, 1989) and Carlos et al. (1990) have provided chemical data on zeolites and clays found in fractures.  In general, the zeolites found there are similar in composition to zeolites present in the matrix adjacent to a given fracture sample, although exceptions have been noted.  Analytical data on the surface compositions of most of the other mineral phases listed in Table 6 are essentially nonexistent.  The actual surface structures (for example, defects and pits) of minerals in Yucca Mountain tuffs are also essentially unknown.